Low HAP Materials

TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

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Report Documentation Page

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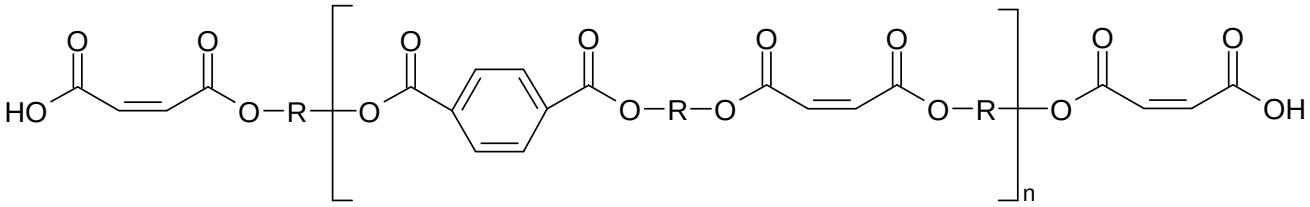
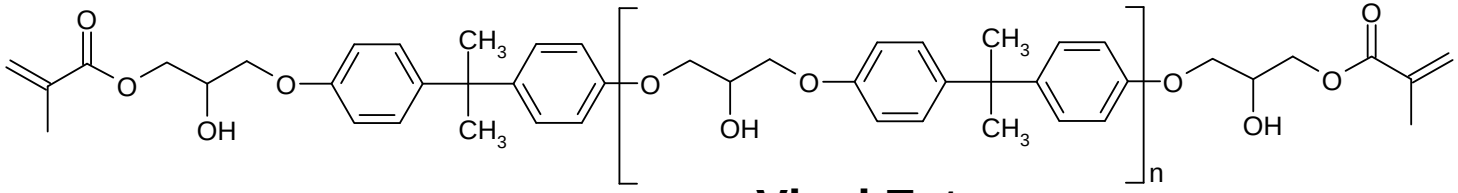
Outline

- **Fatty Acid Vinyl Ester Resins/Composites with low hazardous air pollutant contents**
- **Other low HAP composite resin developments**
- **Low HAP Adhesives and Sealants**

UPE and VE Resins

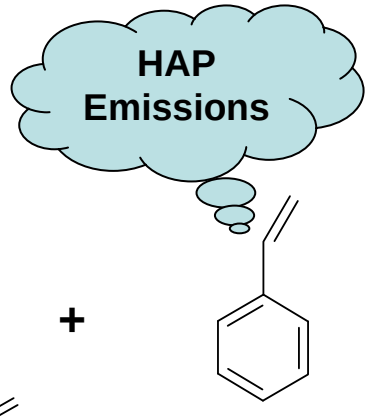
Unsaturated Polyester





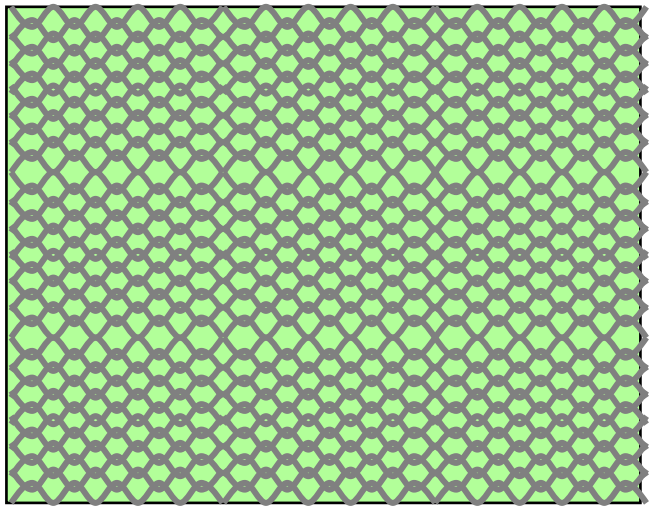
Vinyl Ester

+



Styrene

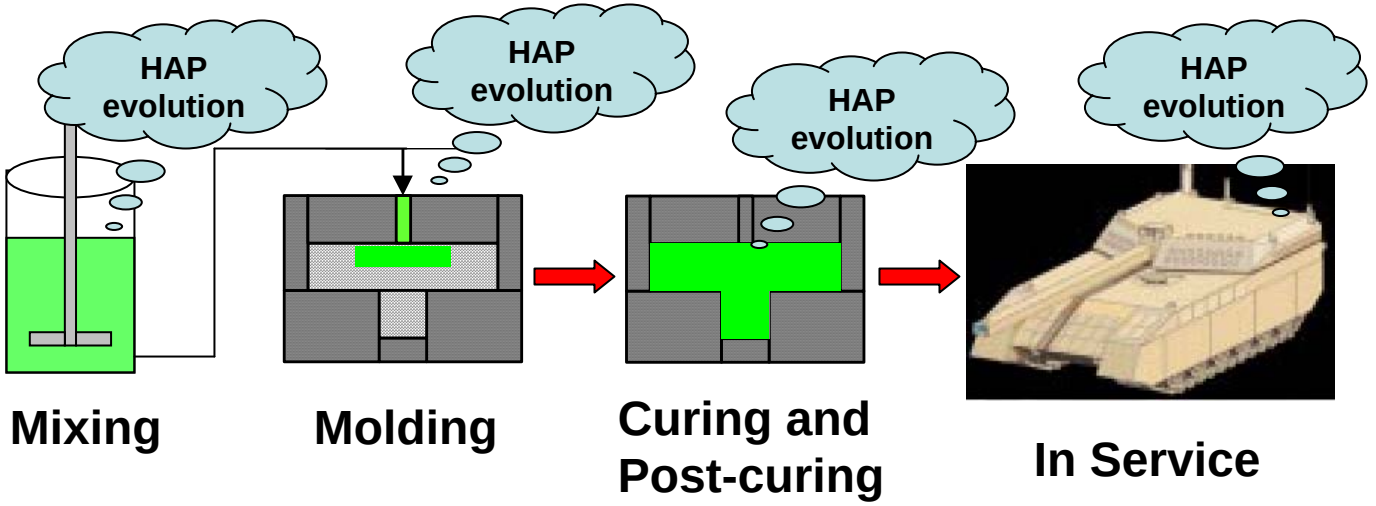
Initiator + Heat



Thermosetting Polymer

VOC/HAP Emissions

- **Liquid resins used in molding large-scale composites are a significant source of Hazardous Air Pollutants (HAP)**



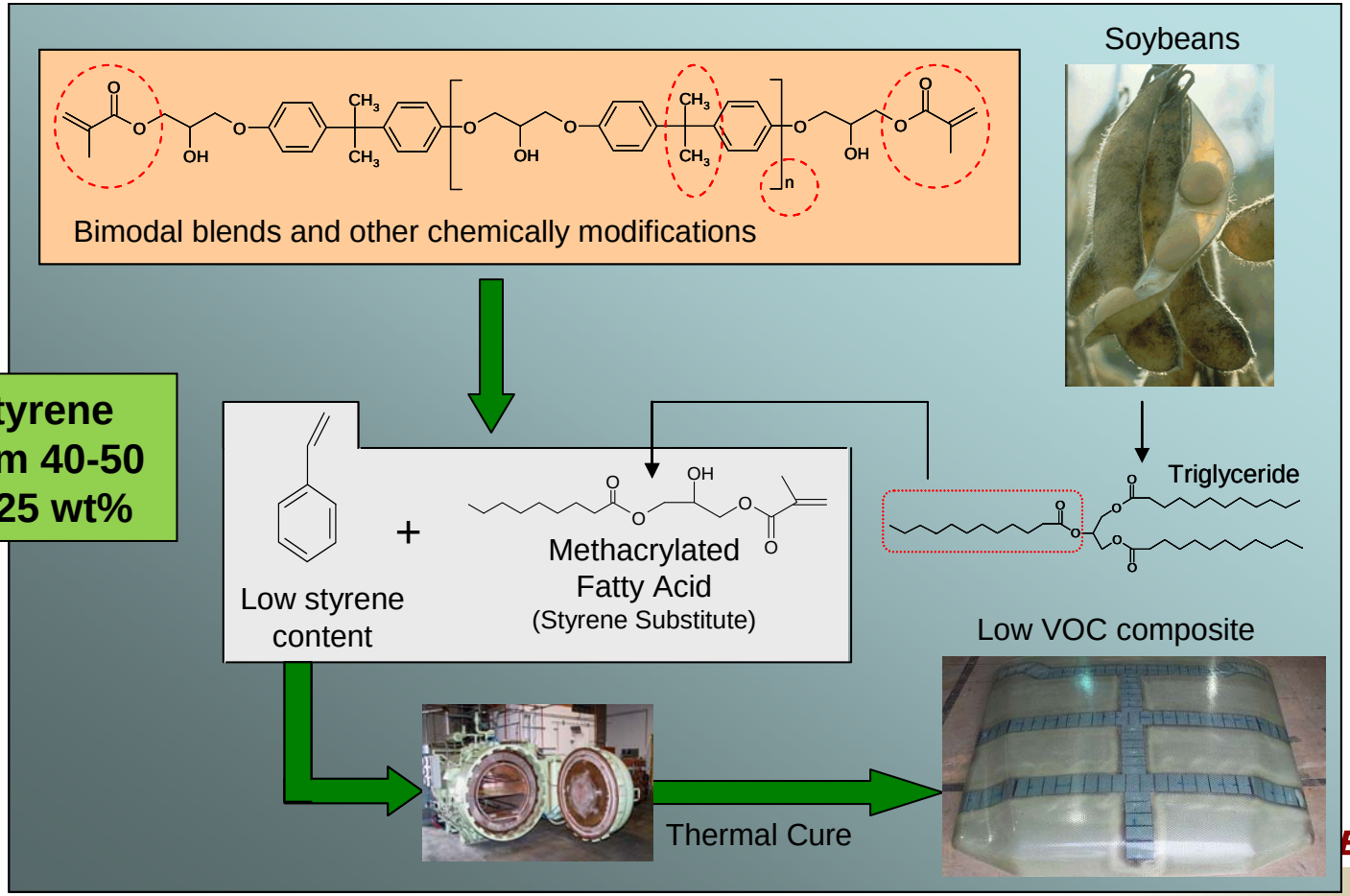
Composites industry consumes 9% of the styrene, but accounts for 79% of styrene emissions

- **EPA - Reinforced Plastic Composites National Emissions Standards for Hazardous Air Pollutants (NESHAP)**
  - **Executed and legally enforceable as of April 28, 2003**
  - **Regulation imposes a substantial barrier to fielding and development of new composite technologies for military platforms.**

Technical Approach

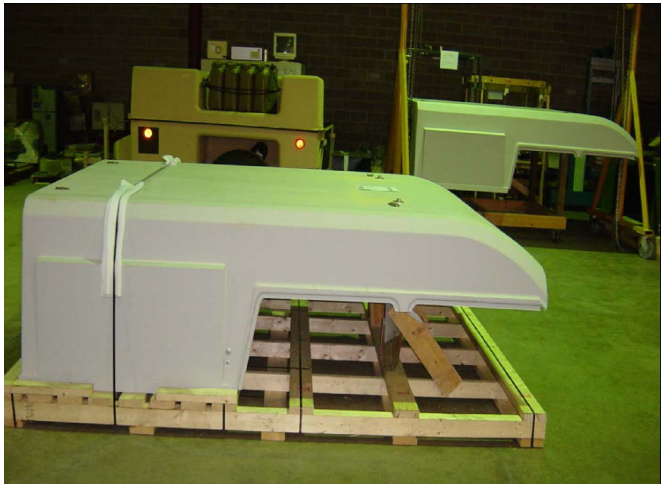
- **Use fatty acid monomers to reduce styrene content.**
  - **Non-volatile**
  - **Maintain low viscosity**

FAVE: Fatty Acid-Based Vinyl Ester Resin



Reduce styrene content from 40-50 wt% to 10-25 wt%

Demonstration Platforms



HMMWV ballistic hardtop

HMMWV transmission container

M35A3 hood

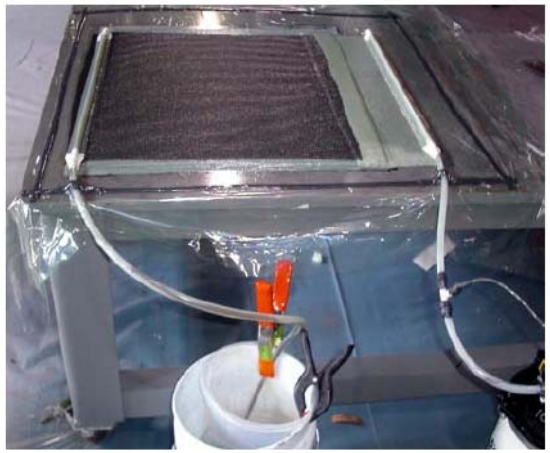
T-38 dorsal cover

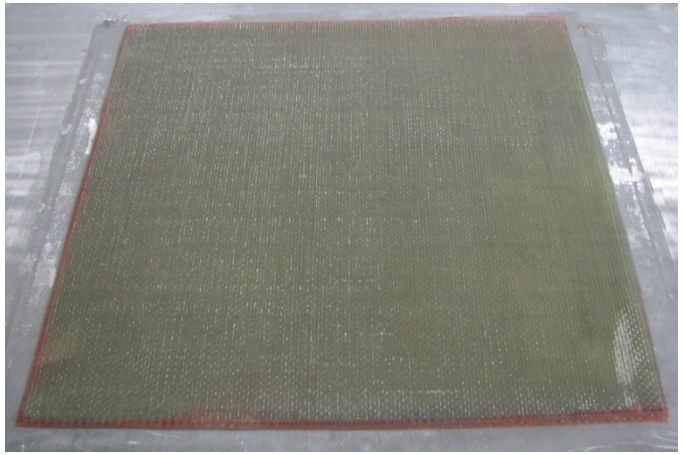
MCM composite rudder

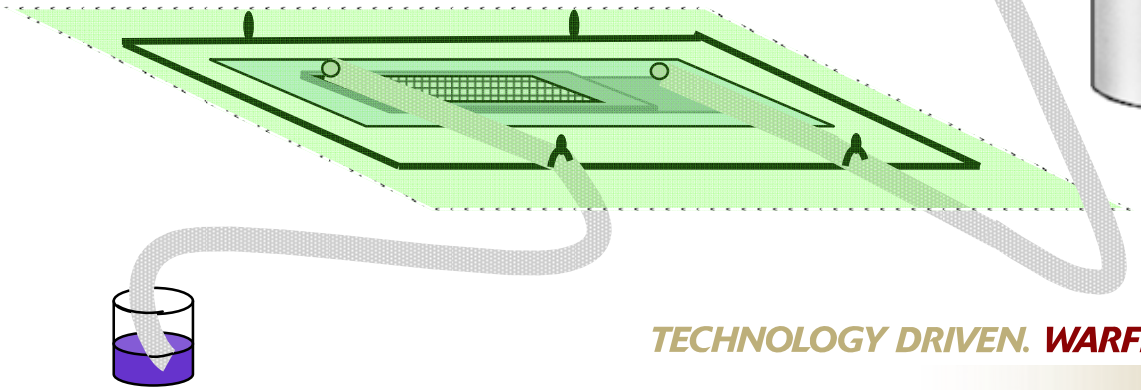
M939 hood

Composite Manufacturing

- Vacuum Assisted Resin Transfer Molding (VARTM)
  - Cured at room temperature using CoNap and DMA catalysts, 2,4-P inhibitor, and Trigonox initiator
  - Post-cured for 2 hours at 130°C

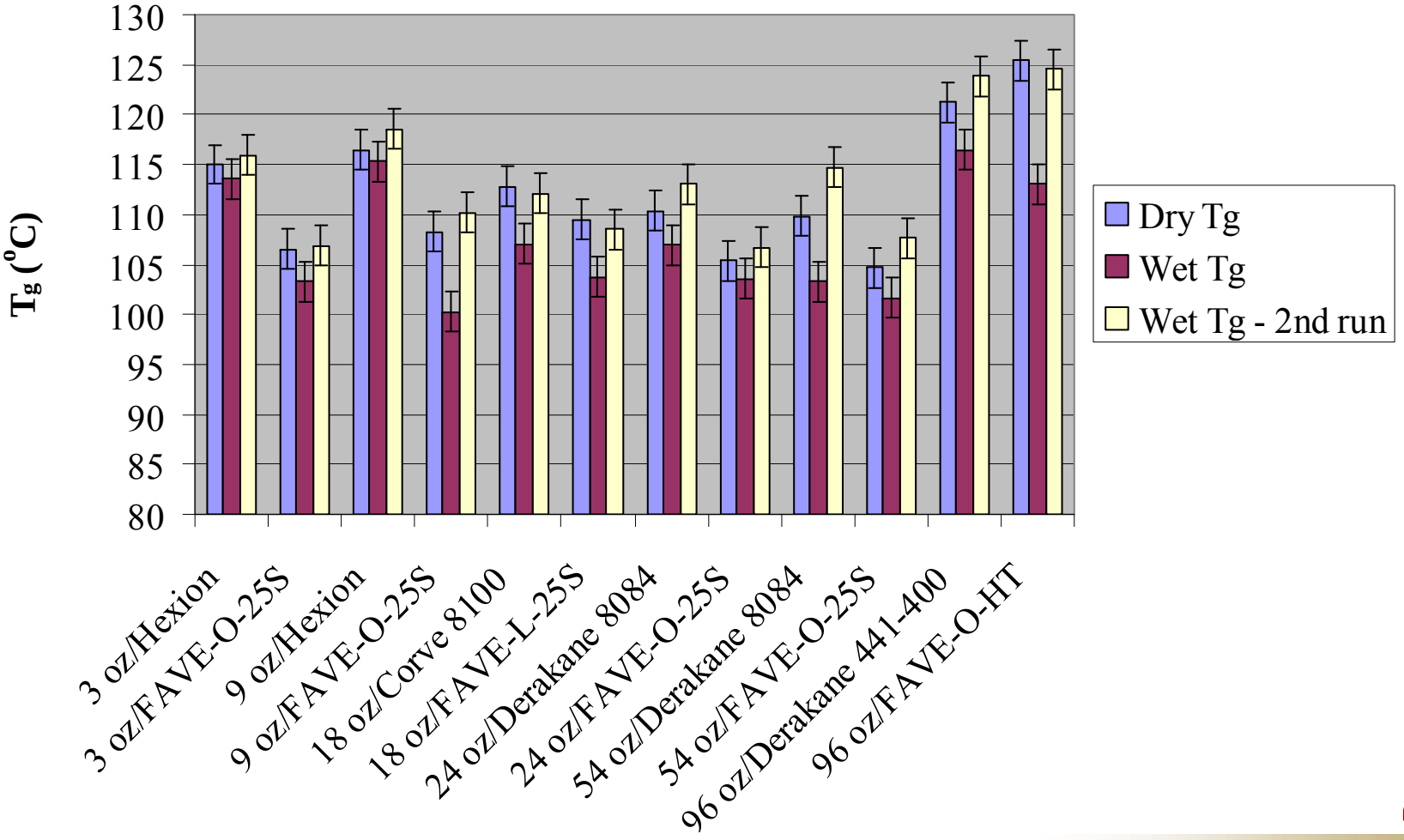






Glass Transition Temperature (Tg)

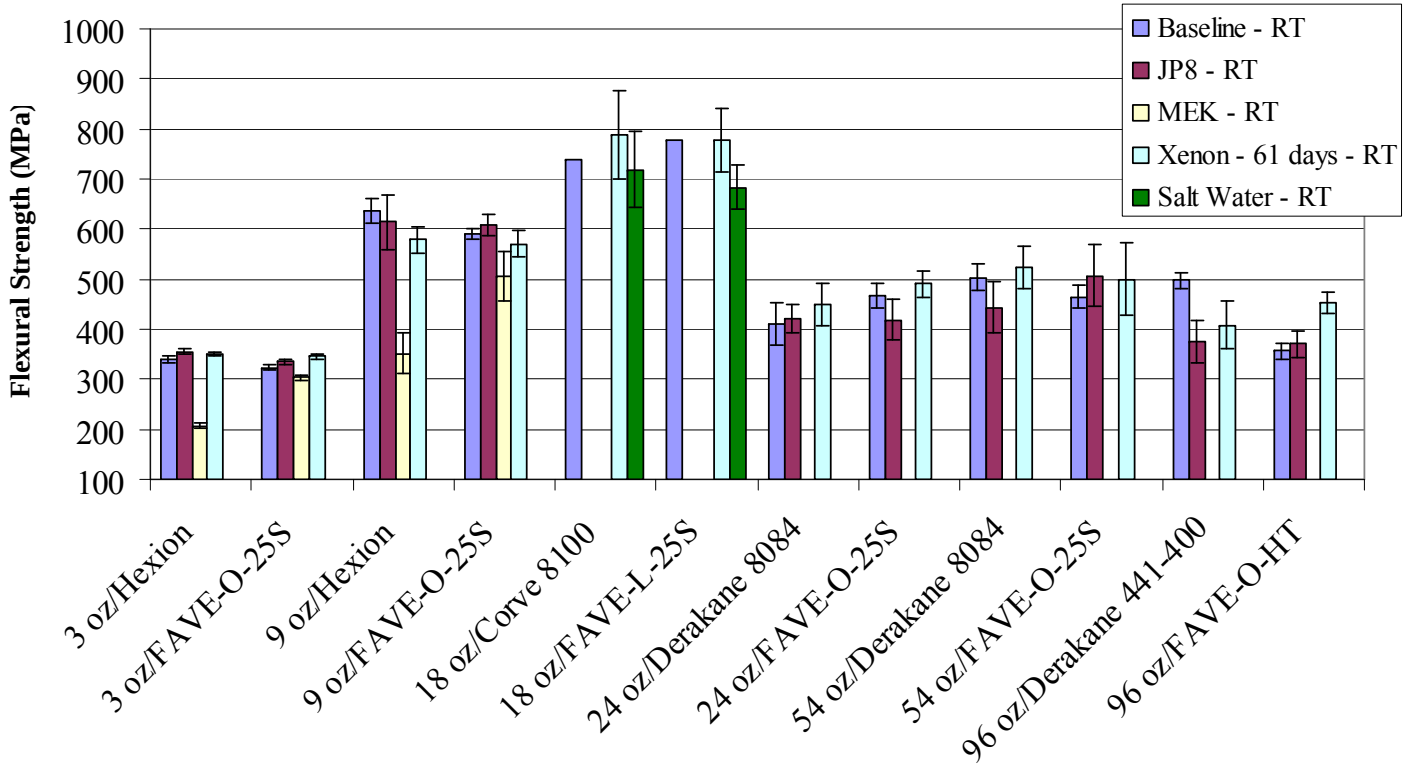
- **Very similar Tg for FAVE composites relative to commercial composites.**
- **Tg decreases as a result of water ingress**



USED.

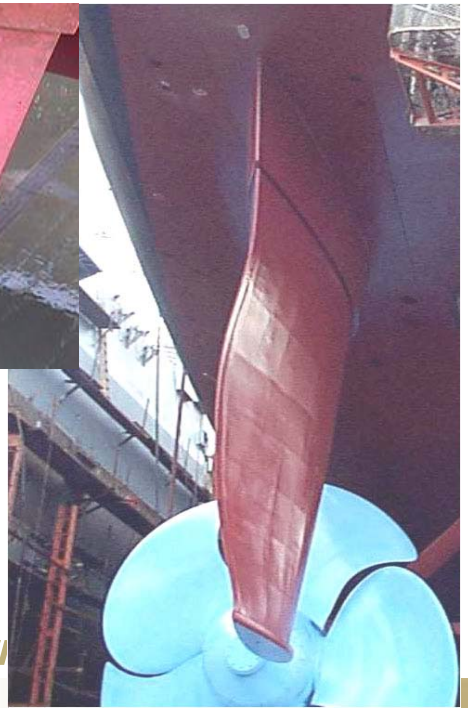
Environmental Aging

- **Water (DI and salt) and Xenon weathering:**
  - **Tg, strength, and modulus reduced for wet samples.**
  - **FAVE and commercial resins performed similarly.**
- **Solvents/fuel immersion:**
  - **Tg , strength, and modulus reduced for wet samples.**
  - **FAVE performed similarly or out-performed commercial resins.**



Navy Composite Rudders

- Straight rudder (MCM)
- Composite twisted rudder (CTR) – DDG51 and DDG1000
- Easier to fabricate and less cavitation than steel twisted rudders
- Composite rudder on MCM-9 has good success after 6 year fielding trial



Demonstrate/Validate low VOC/HAP formulations for one of these applications

MCM Rudder Fabrication

Completed rudder

Trailing Edge

Leading Edge

- 1 hr resin infusion
- Rudder fabrication done by Structural Composites, Inc., overseen by NSWCCD

MCM Rudder Fabrication

- Some excess resin pockets (wrinkling)
- One rudder will be demo piece.
- The other rudder was sectioned and is being analyzed by NSWCCD to validate the structure.

Army Tactical Vehicle Replacement Parts

- Corrosion issues with M35A3
- Sheet molding compound (SMC) HMMWV hood has poor performance
- Transmissions damaged in shipment without good packaging
- Test demo parts
  - Flexural, impact, cyclic load, High T, etc.

HMMWV Transmission Container

- Container designed to protect HMMWV transmissions from damage during shipping
- Container must have:
  - desiccant port
  - lifting handles
  - latches – no accidental opening
  - humidity indicator
  - pressure relief valve
  - drainage plug
  - forklift and pallet jack tine pockets
- Container designed by CCM/Sioux Manufacturing Corp. (SMC)
- Container manufactured by SMC

HMMWV Trans. Container: Commercial Prod.

Infusion

- According to SMC, resin infused as well or better than incumbent resins
- Resin required only 30 minutes for infusion

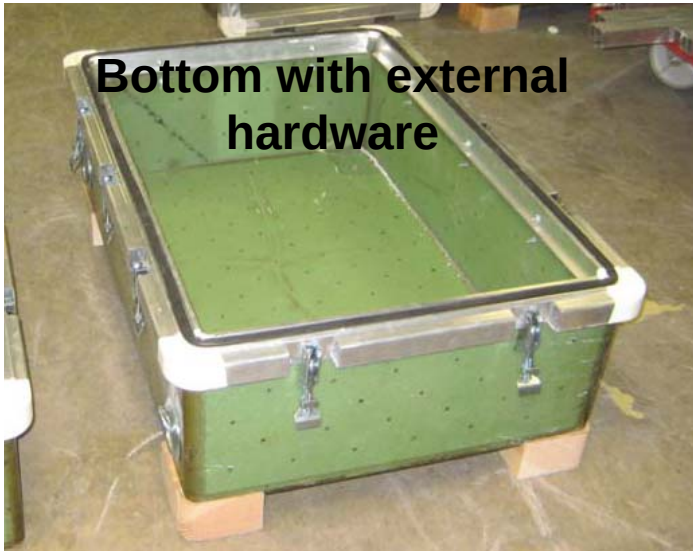
HMMWV Trans. Container: Commercial Prod.

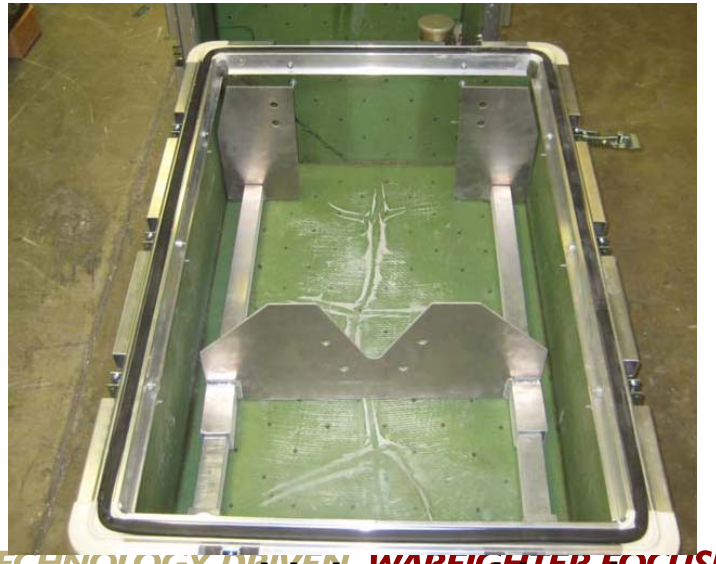
Infused Top

Infused Bottom

HMMWV Trans. Container: Commercial Prod.

Top with hardware





Bottom with internal hardware

HMMWV Trans. Container: Commercial Prod.

Assembled Container

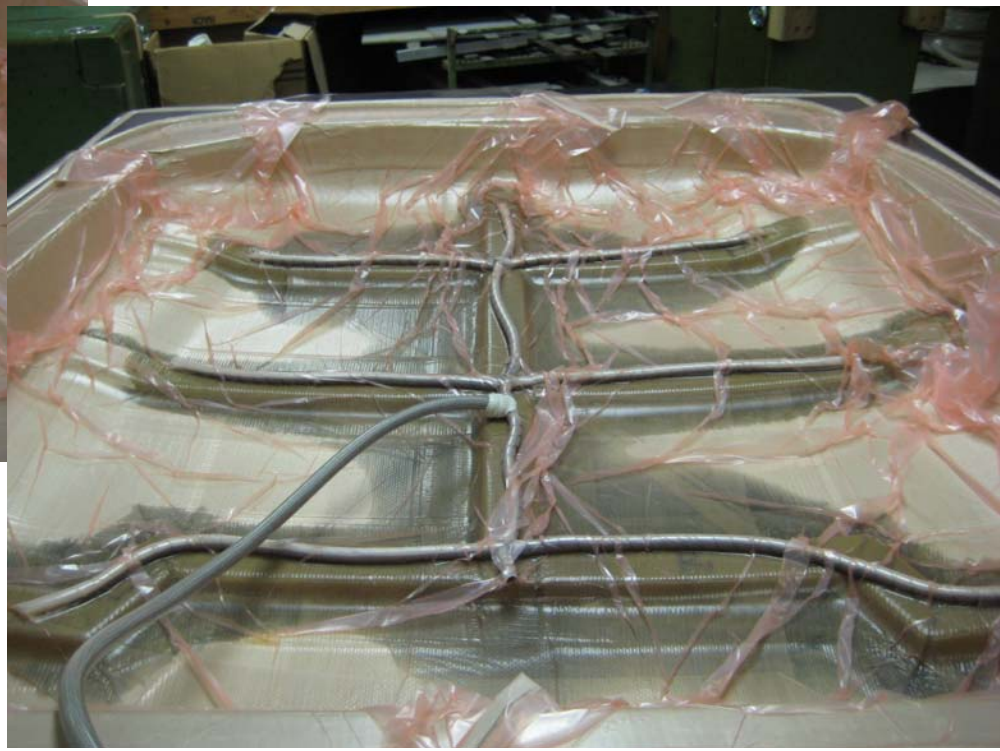
HMMWV Transmission Container

- Drop tests
  - Rotational Edge Drop Test per ASTM D6179 Method A
  - Rotational Corner Drop Test per ASTM D6179, Test Method B
  - Unsupported free fall drop test per ASTM D6179 Method D
  - Tipover Test per ASTM D6179, Method G
  - Vibration Test per ASTM D999 Test Method B
  - Later Impact Test per ASTM D880, Procedure B, 179, Test Method B
- Leakage test
  - Pressurize to 10 kPa, $\Delta P < 0.2$ Pa in 30 minutes
  - Pull a vacuum of 7 Pa, $\Delta P < 0.2$ Pa in 30 minutes
- Validation tests are nearly completed at CCM
- Fielding trials are in progress at RRAD

Commercial Production – M35A3 Hood

- **M35A3 Truck hood manufactured by SMC**

Bagged Hood



After 10 min of infusion

Commercial Production – M35A3 Hood

Final Hood

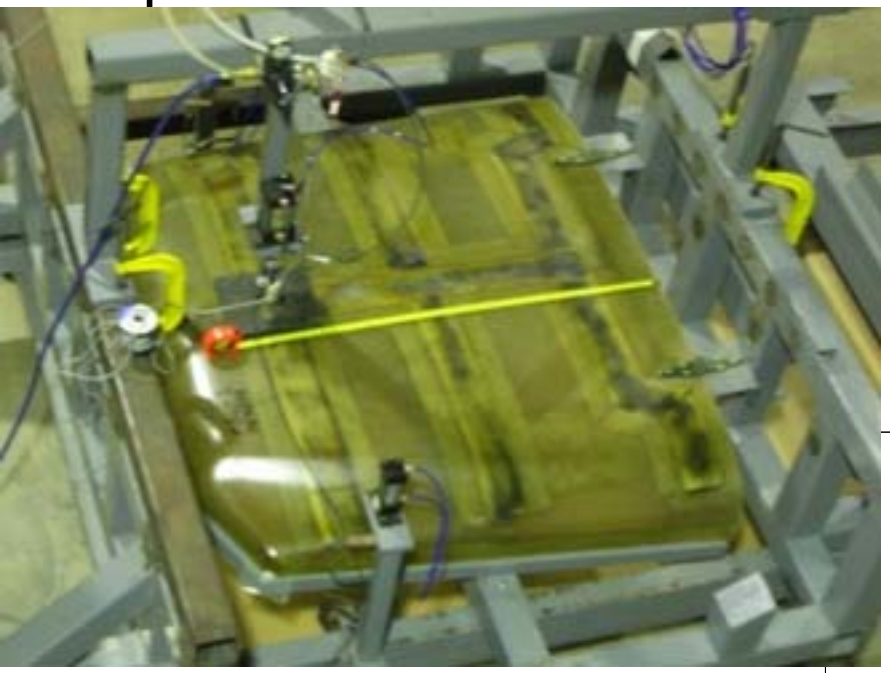
- According to SMC, resin infused as well or better than incumbent resins
- Resin required only 51 minutes for infusion

Final Part

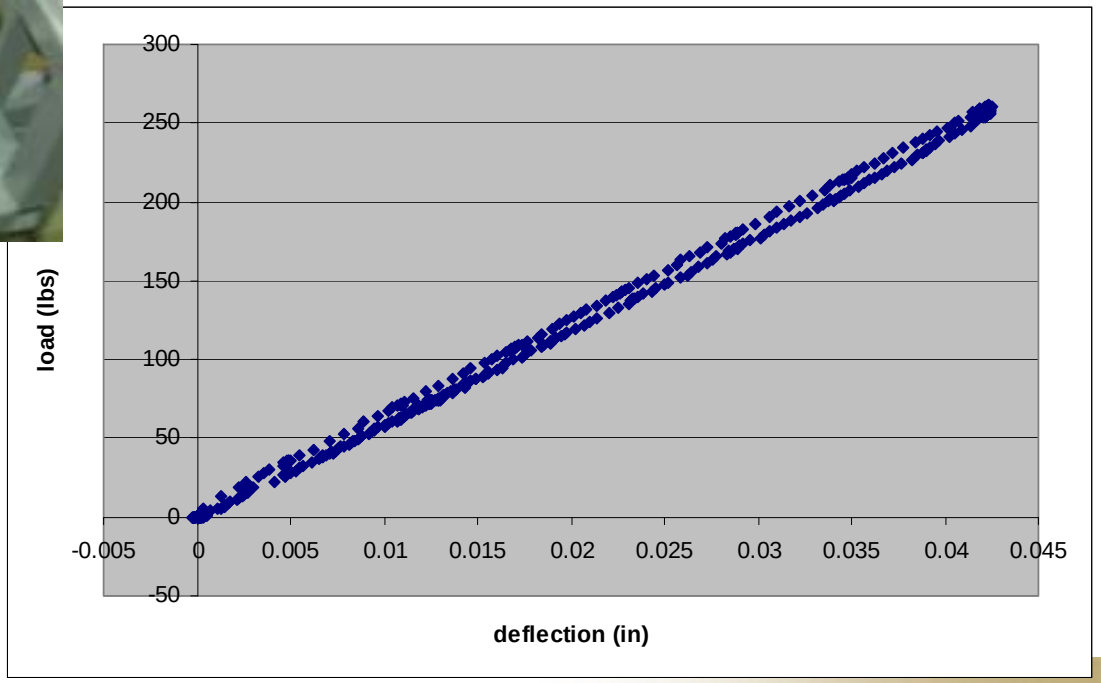
- **Low HAP hood painted with low VOC/HAP water-dispersible CARC (MIL-DTL-64159)**

M35A3 Hood Validation – Top Loading

Top Front Load



- **No permanent deformation.**
- **No separation of reinforcements from the hood.**
- **No cracks.**
- **Test passed.**



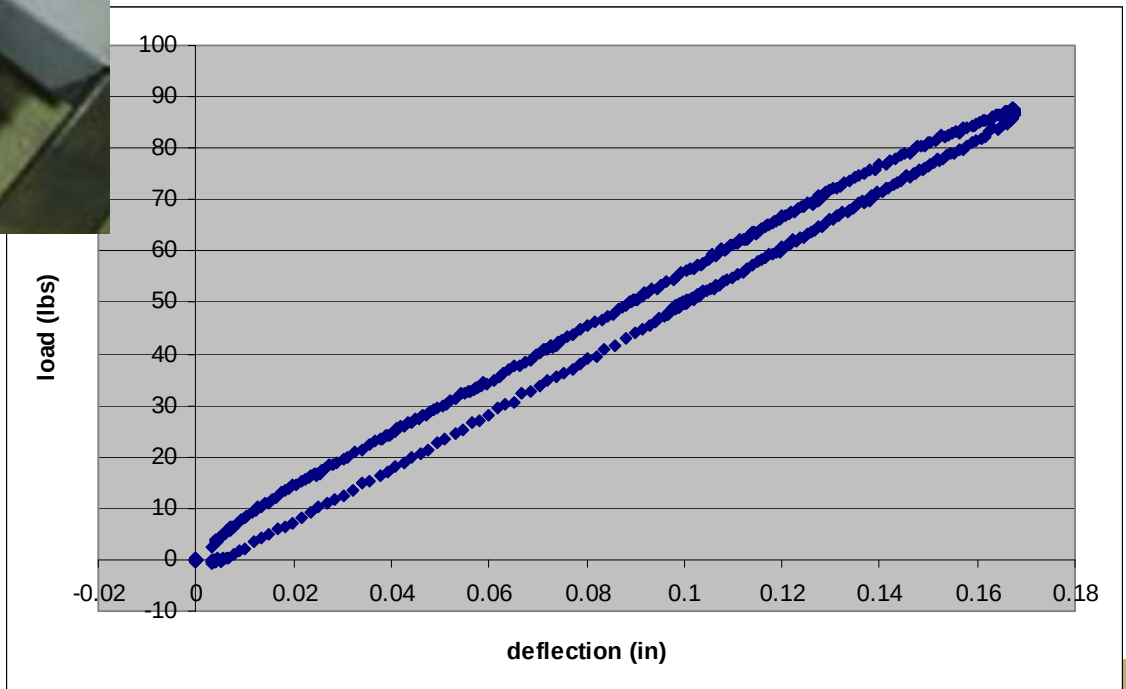
- **Elastic deflection 0.04” at 250 lbs.**
- **Much less than 0.50” allowed**
- **Test passed.**

M35A3 Hood Validation – Corner Lifts

Driver Corner Lift

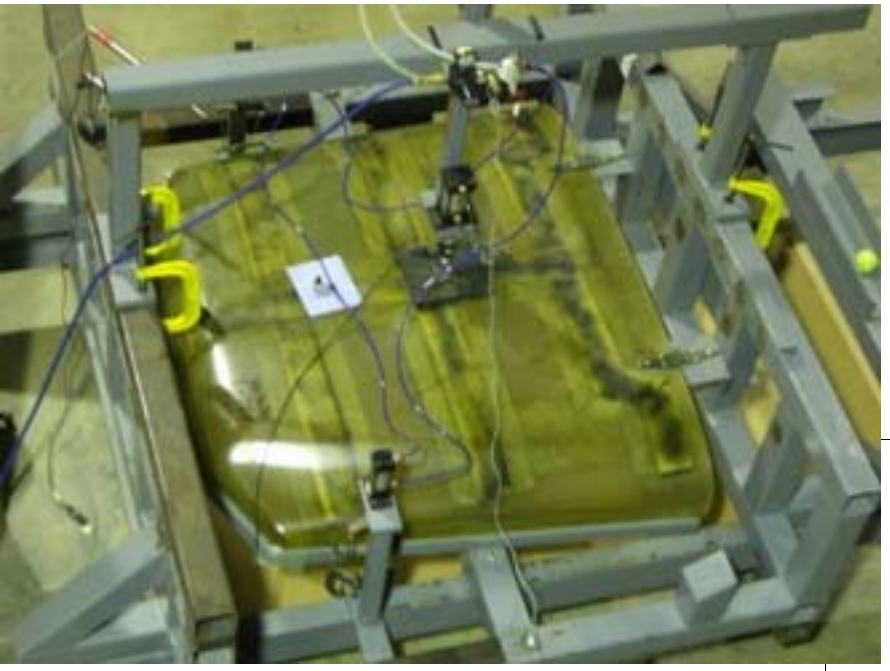
- **No permanent deformation.**
- **No separation of reinforcements from the hood.**
- **No cracks.**
- **Test passed.**

- **Elastic deflection 0.16” at 85 lbs.**
- **More than 50 lbs required to lift corner 0.375”**
- **Test passed.**



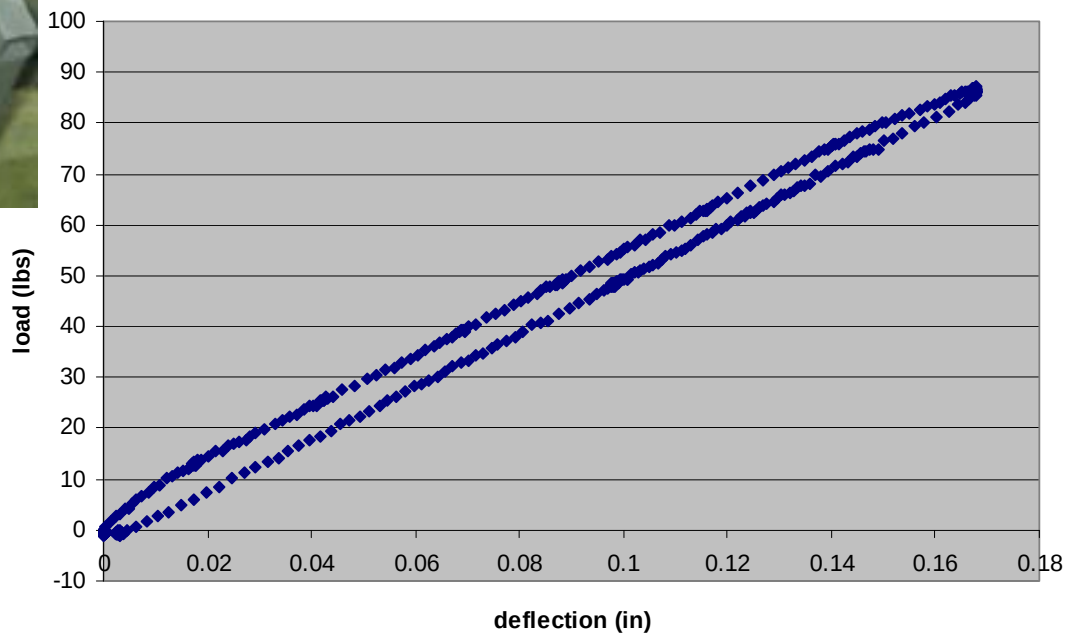
M35A3 Hood – Cyclic Handle Loading

Cyclic Handle Load



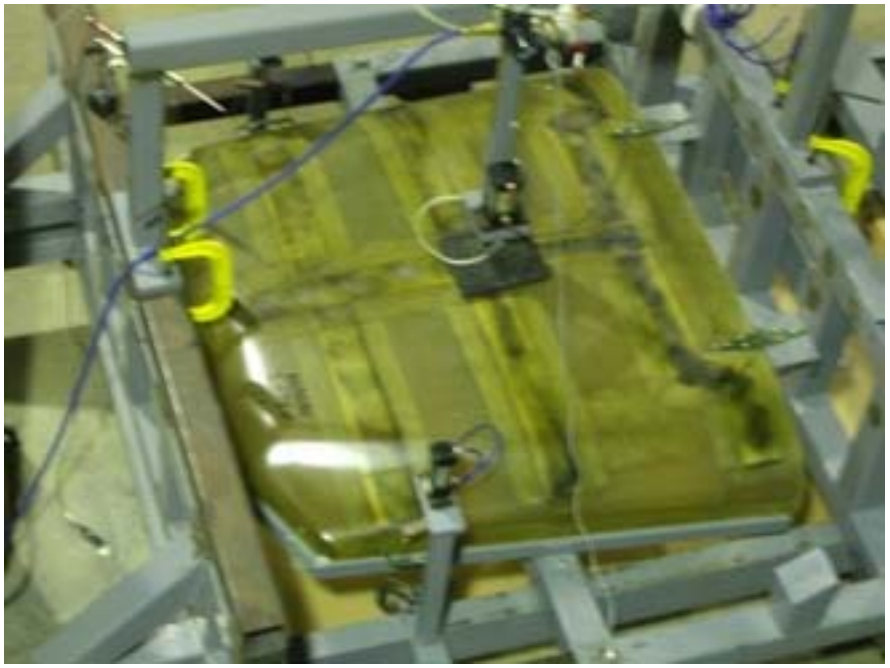
- Elastic deflection 0.16” at 85 lbs.
- More than 50 lbs required to lift corner 0.375”.
- No significant change in stiffness after cyclic loading.
- Test passed.

- No permanent deformation.
- No separation of reinforcements from the hood.
- No cracks.
- No broken fibers visible on areas where the hood contacts the fixture
- Test passed.



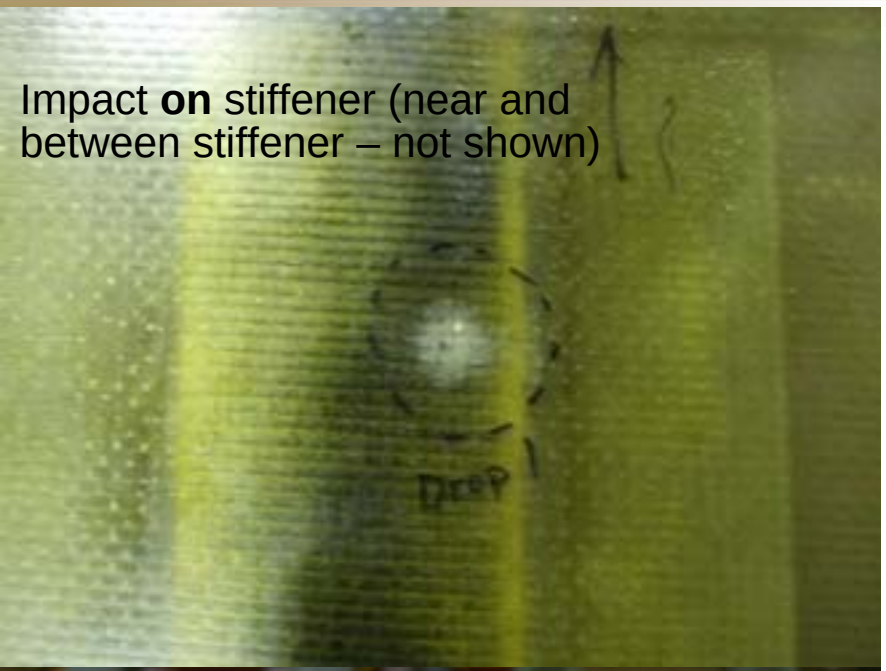
M35A3 Hood Validation – Durability

Durability (cyclic loading followed by load deflection)



- **No permanent deformation.**
- **No separation of reinforcements from the hood.**
- **No cracks.**
- **No broken fibers visible on areas where the hood contacts the fixture**
- **Test passed.**

M35A3 Hood Validation – Impact



Impact **on** stiffener (near and between stiffener – not shown)

Impact on large radius corner

- **No permanent deformation.**
- **No separation of reinforcements from the hood.**
- **No cracks.**
- **Test passed.**

Impact between stiffeners

M35A3 Hood Validation

- **FAVE M35A3 passed all validation testing**
- **FAVE M35A3 performed nearly identically to baseline epoxy M35A3**

- **Hoods installed on M35A3 trucks at RRAD for field testing**

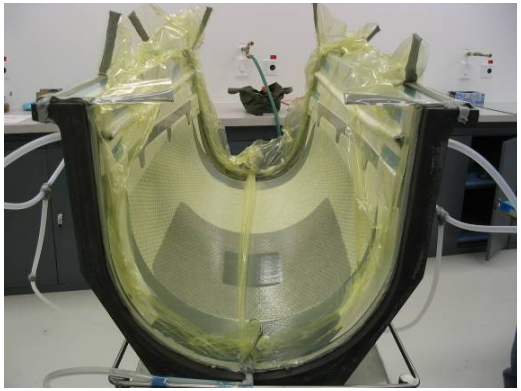
FAVE-O-25S Ballistic Performance

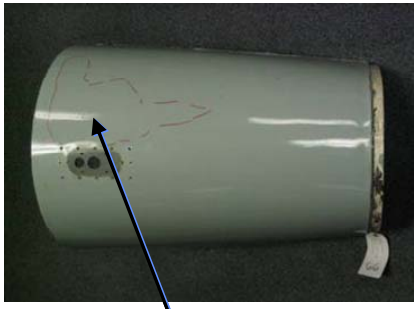
- **Performance assessed in all-composite panel form**
  - **100oz 3TEX 3WEAVE S2 Glass Construction**
  - **4 ply panel for NIJ IIIa (44 magnum) equivalent**
  - **12 ply panel for NIJ III (7.62 M80 Ball) equivalent**
  - **Compared directly to Derakane 8084 VE Resin – slightly different fabric architectures (24oz faces on 8084 panel) and FCS2 Epoxy**
- **FAVE resin had similar or better performance with 44 mag. and M80 threats relative to both commercial resins**

T-38 Dorsal Cover

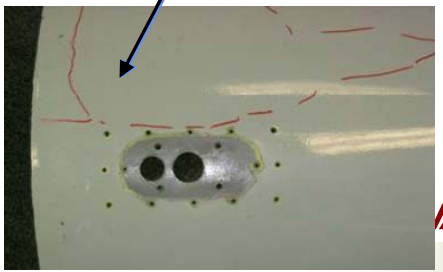
- 400 planes upgraded to ‘C’ model
- Upgrade caused pre-mature failure
- AFRL developed new VARTM dorsal cover
- Requirements
  - Drop-in replacement
  - Thermal, mechanical, electrical, solar

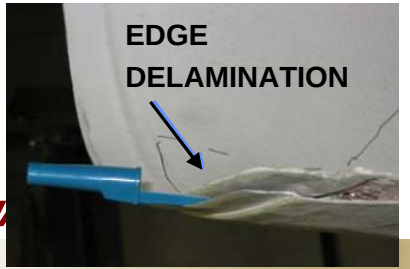
Demonstrate/Validate low VOC/HAP formulations for one of these applications





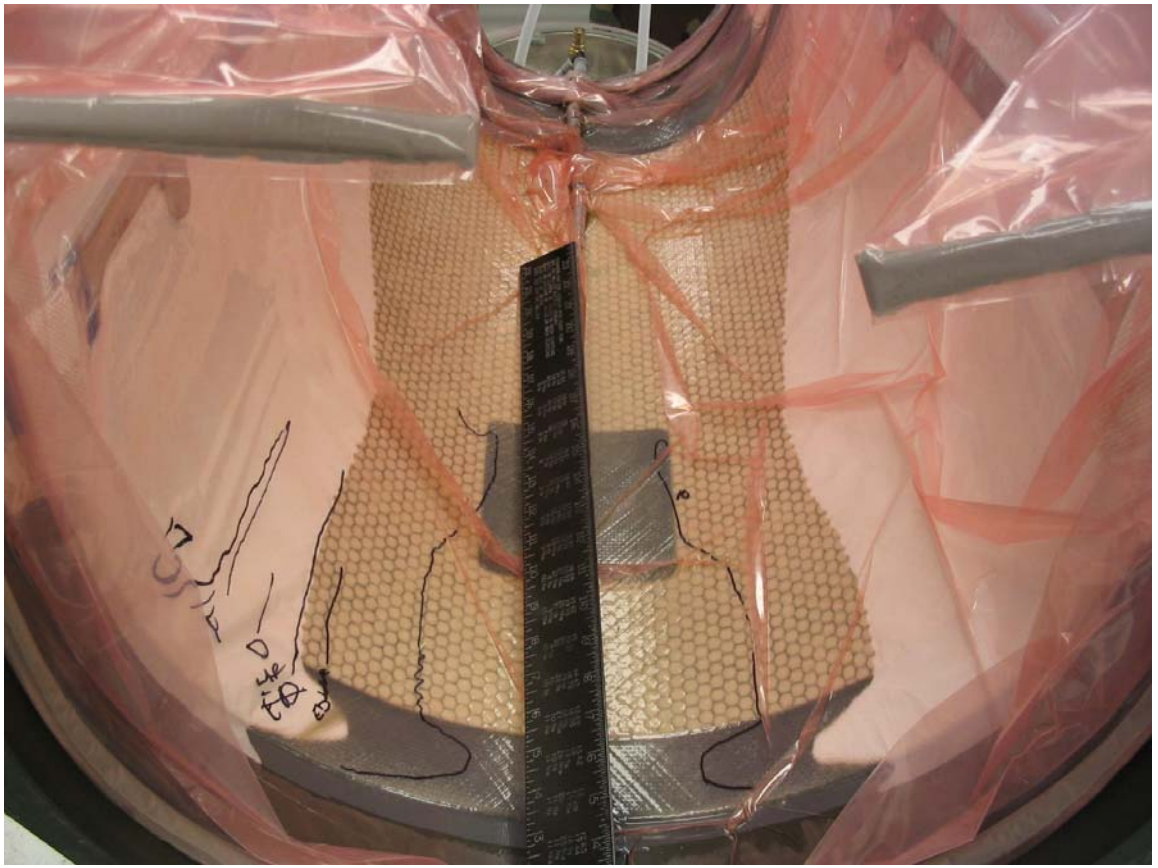
DISBOND





Dorsal Cover Demonstration – Initial Failure

- **Short-shot infusion of T-38 dorsal cover**
- **FAVE-L resin viscosity was too high**
- ***Used FAVE-L-25S instead and solved processing issue***
- **Current resin uses 47% styrene – substantial reduction**

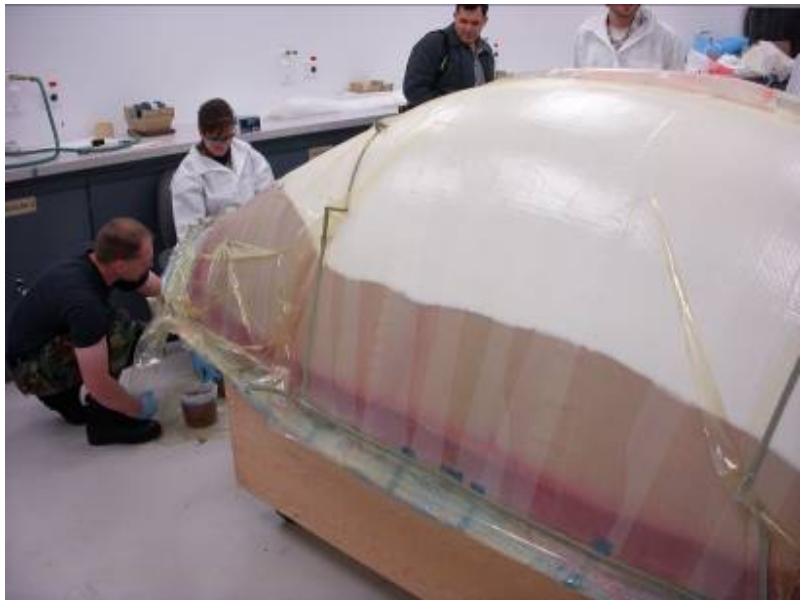


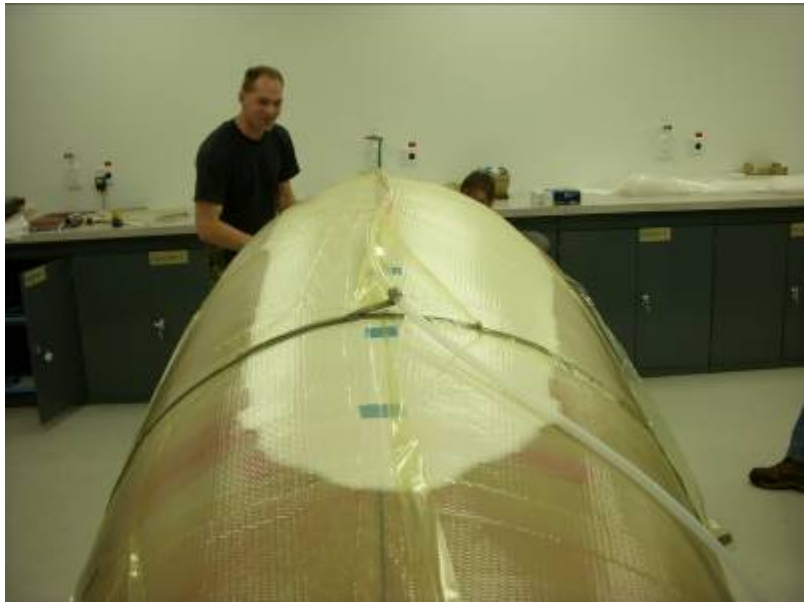
Air Force Progress

- ✓ Manufactured and validated composite panels
- ✓ Manufactured T-38 dorsal cover
- Validation of structure will take place in the coming months

- AFRL expanded demonstration to F-22 canopy cover
  - Protects canopy against overspray during painting operations
  - Far easier and quicker than taping a cover in place
  - Used FAVE-L-25 resin to manufacture demo part

Infusion of F-22 Canopy Cover





F-22 Canopy Cover Prototype

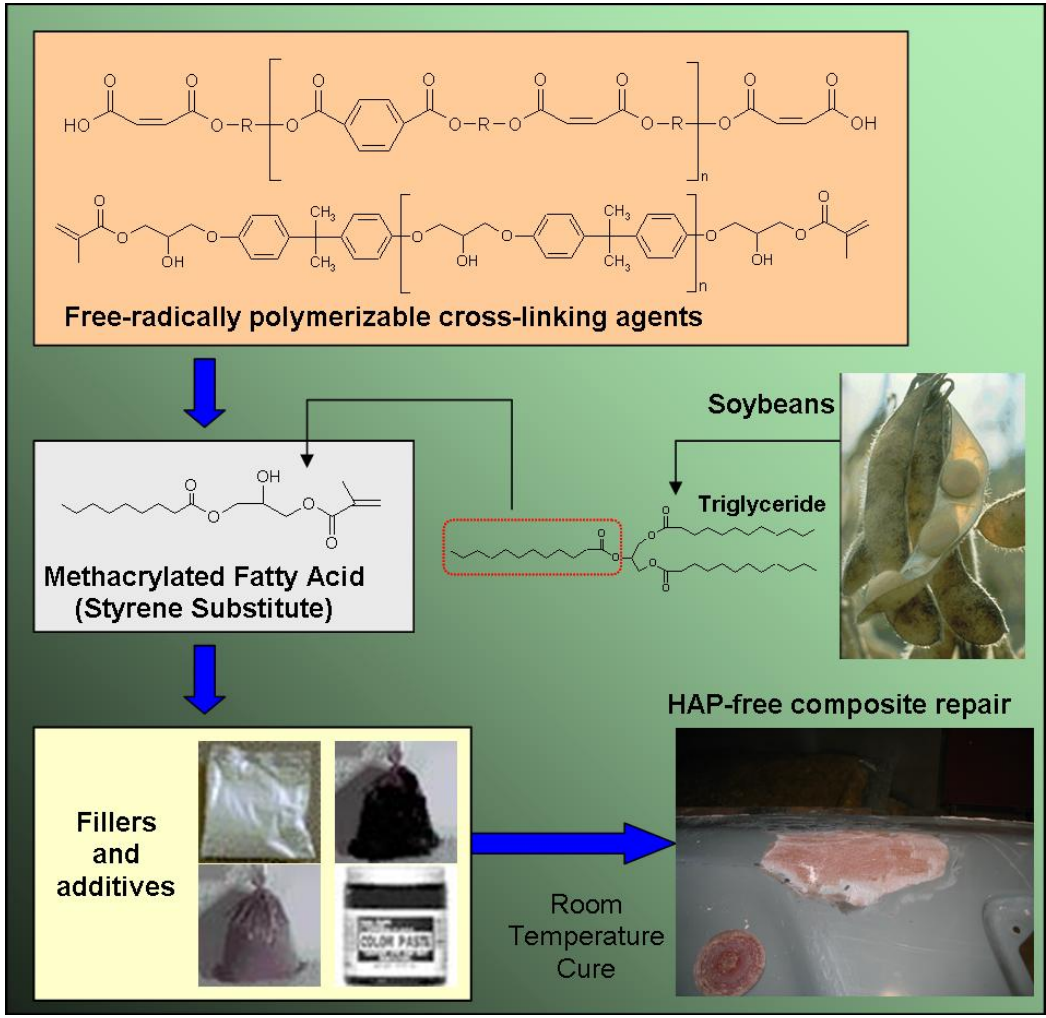
Life Cycle Analysis

- Current estimated MFA price range: $1.23-$2.85/lb
- Cost of fatty acid VE resin is $0-$1.16 higher per pound
  - Depends on resin formulation and scale
- Cost for emissions capture and treatment avoidance is $1.13 per pound of resin
- Cost of carbon footprint is $0.30 per pound of resin.

- FAVE resins are more cost effective
- FAVE resins have a lower environmental impact
- FAVE resins have recently been licensed by Dixie Chemicals

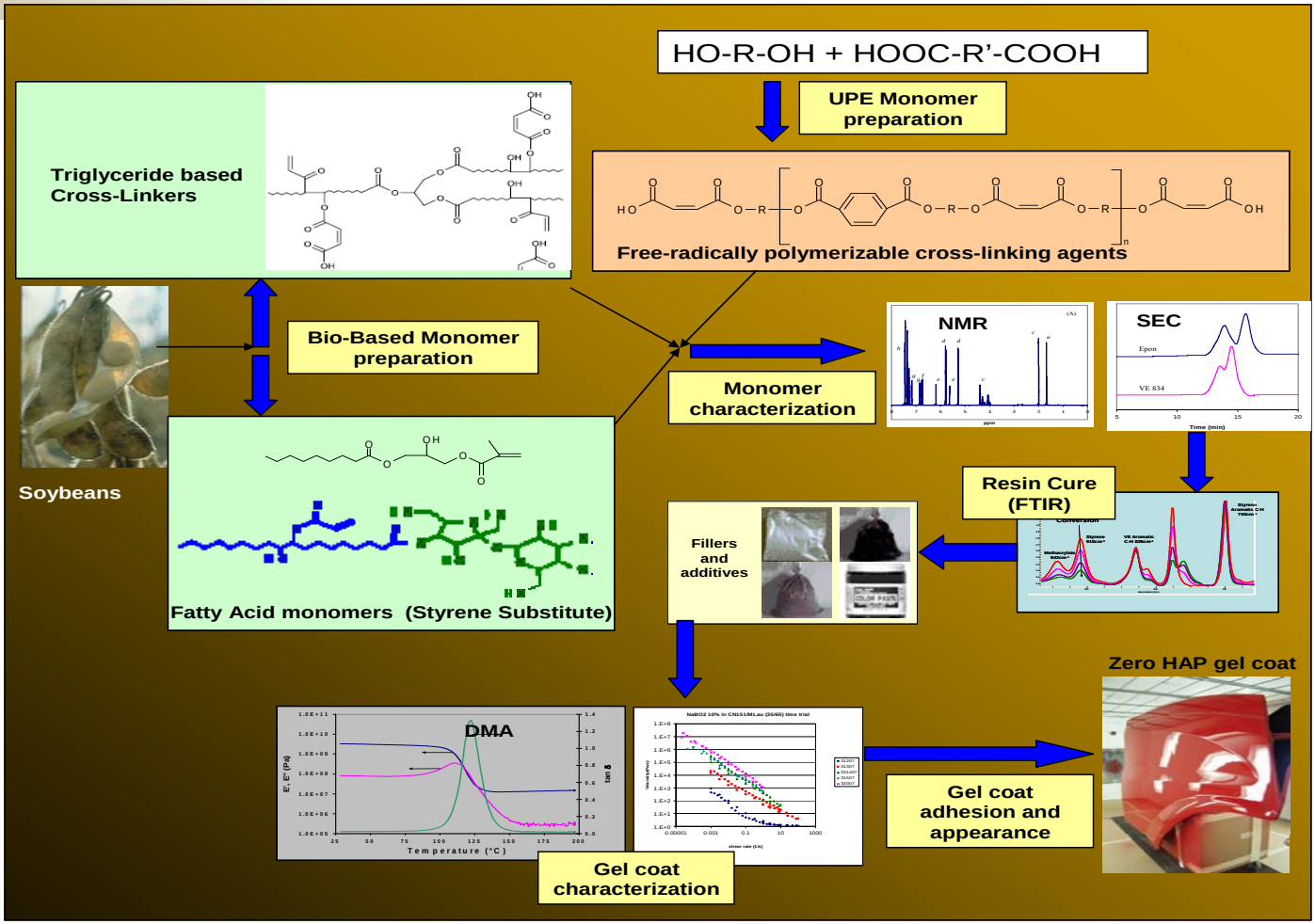
HAP-Free Repair Resin Similar to Bondo

- **Binder**
  - **Use MFA to replace styrene**
  - **Use VE and/or UPE cross-linkers**
- **Fillers**
  - **Use similar fillers/contents as in BONDO**
- **Promoters**
  - **Dimethylaniline**
- **Curing agents**
  - **Use BONDO hardeners**
  - **Formulate hardeners**



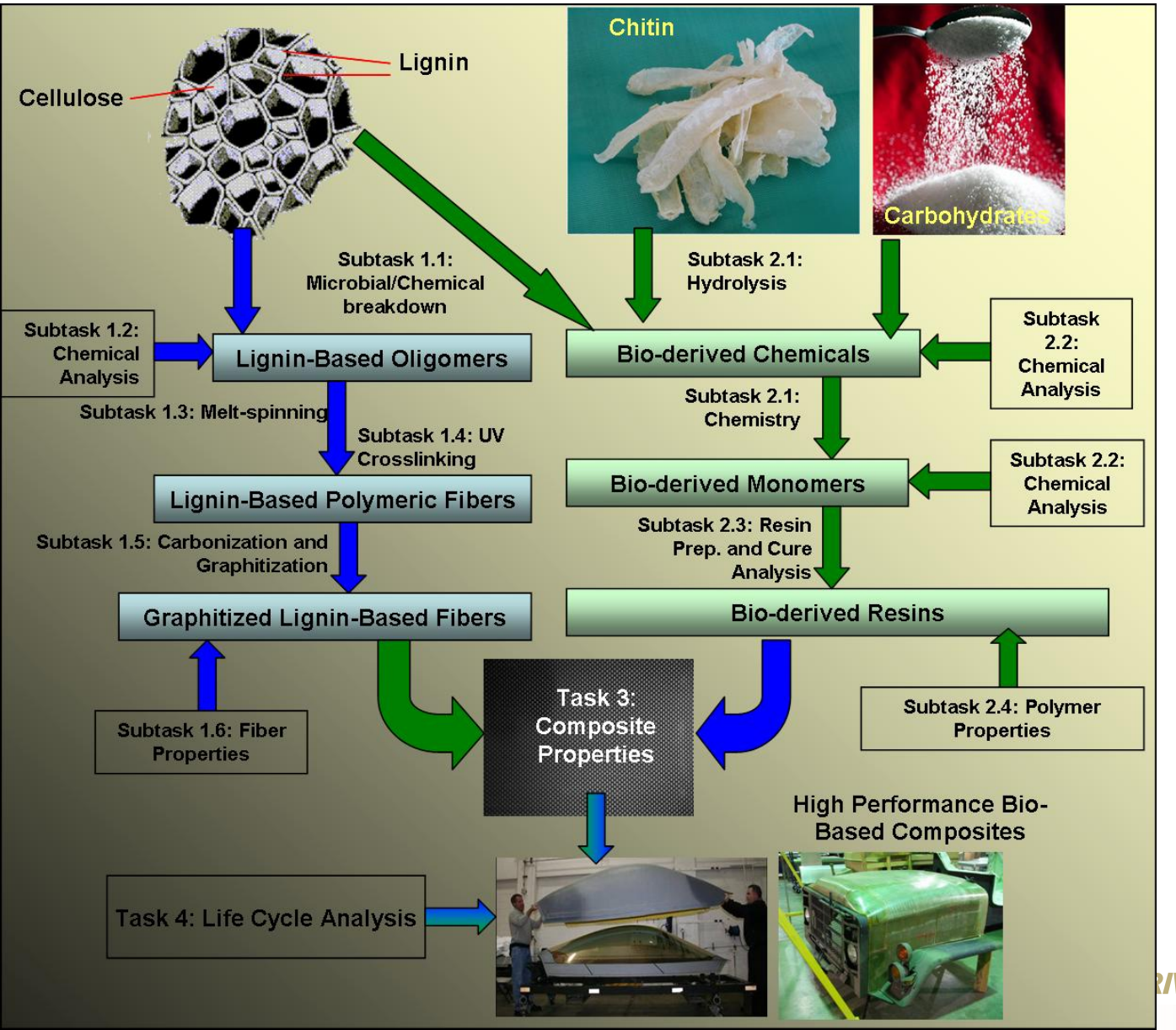
HAP-Free Bio-Based Gel Coats

- Gel coats used to provide smooth surface for composites
- Gel coats emit large HAP percentages.



- Use maleinized triglycerides to replace UPE
- Use novel bio-based reactive diluent to replace styrene

Bio-Based Carbon Fibers and Thermosetting Resins



- SERDP proposed new start, FY10
- Microbially breakdown lignin into oligomers that can be melt spun and carbonized
- Modify renewable resources and bio-based chemicals to make bio-based monomers
- Assess, fiber, resin, and composite properties

SPOTA – Tank Tread and Road Wheel Rubber to Metal Bonding

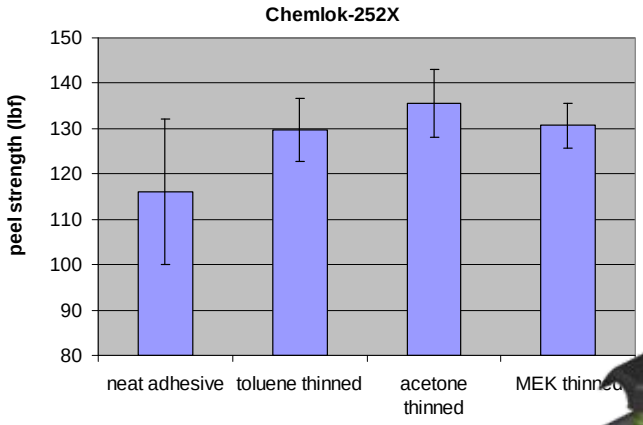
Background:

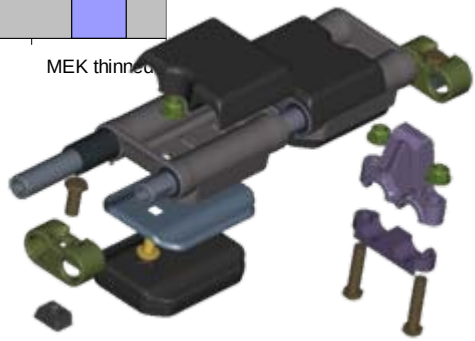
RRAD currently uses adhesives for tank treads and road wheels that contain very high HAP contents. The Defense Land Systems and Miscellaneous Equipment (DLSME) NESHAP is requiring reduced HAP in all DoD coating operations.

Objectives:

•Successfully replace current rubber to metal bonding adhesives with non-HAP alternatives or reduce HAPs through identification of compatible non-HAP thinners.

•Dem/Val best performing candidates at RRAD.





Participants:

U.S. Army Research Laboratory
TARDEC
RRAD
Hayfire, inc.
CTC/NDCEE

Progress to Date:

•Identified non-HAP thinners compatible with existing adhesive systems with similar bench-level performance.

•Identified low HAP alternative adhesives. Bench level testing of these adhesive systems is still in progress.

Benefits:

• Reduced HAP will comply with future EPA regulations, improve worker health, and improve mission readiness.

POC: John J. La Scala (410)-306-0687

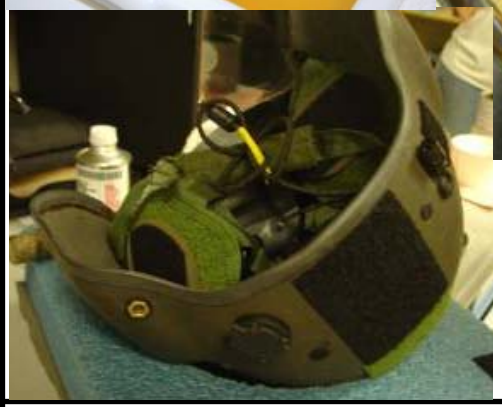
SPOTA – Contact Adhesive

Background:

The Defense Land Systems and Miscellaneous Equipment (DLSME) NESHAP will require reduced HAP in all DoD coating operations. Rubber to metal contact adhesives under MMM-A-121 are used on various weapons platforms and produce ~1200 lbs/yr HAP emissions.

Objectives:

•Successfully replace current contact adhesives with non-HAP alternatives.



Participants:

SPOTA
U.S. Army Research Laboratory,
AMCOM G-4
Fort Rucker
Hayfire, inc., CTC/NDCEE

Progress to Date:

- Identified 3M Scotchweld 847 as a zero HAP, zero VOC alternative
- Laboratory testing showed similar performance relative to baseline
- Dem/val ongoing at Fort Rucker on blackhawk nose door seal and aviation helmet

Benefits:

- Reduced HAP will comply with future EPA regulations, improve worker health, and improve mission readiness.
- Improved performance.

POC: John J. La Scala (410)-306-0687

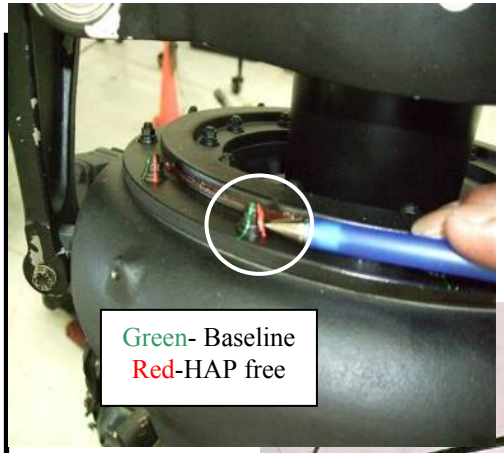
SPOTA – Inspection Lacquer

Background:

The Defense Land Systems and Miscellaneous Equipment (DLSME) NESHAP will require reduced HAP in all DoD coating operations. Inspection lacquers, such as F-900 Torque Seal, contain 20 wt% methanol HAP.

Objectives:

•Successfully replace current inspection lacquer with a non-HAP alternative.



Participants:

SPOTA
U.S. Army Research Laboratory,
AMCOM G-4, Fort Rucker
Hayfire, inc., CTC/NDCEE

Progress to Date:

- Manufactured zero HAP Torque Seal
- Laboratory tested
- Successful dem/val of zero HAP Torque Seal on UH-1 rotor.
- HAP-free product is now listed on the GSA.

Benefits:

- Reduced HAP will comply with future EPA regulations, improve worker health, and improve mission readiness.
- Improved performance.

POC: John J. La Scala (410)-306-0687

Summary

- **Environmentally friendly VE and UPE resins using fatty acid monomers and tailored VE molecular structure**
  - **Effectively reduce HAP emissions**
  - **Comparable resin and composite performance**
- **Variety of other uses for plant oils in composites**
  - **Bio-rubber toughening agent increases toughness dramatically while maintaining T_g and vicosity.**
  - **HAP-free repair resin performs similar to Bondo™ similar**
  - **New generation of environmentally friendly bio-based composites in development.**
- **Low HAP adhesives and sealants.**

- **"Army Green" does not *only* refer to Army colors!**

Acknowledgements

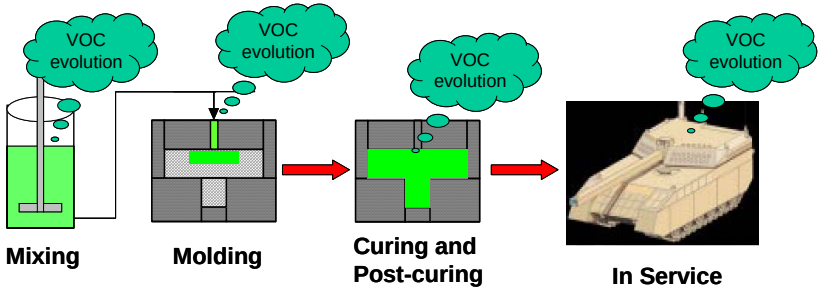
- Army Research Laboratory
  - J.M. Sands, S. Boyd, K. Andrews, T. Glodek, C. Lochner, P. Myers, F. Levine, D. De Bonis, R.E. Jensen, R. Hayes
- Drexel University – Palmese research group
- CCM, University of Delaware
  - S. Anderson, David Fudge, N. Shevchenko, K. Brand
  - Jack Gillespie, Prof. Wool Research Group
- NSWC, Carderock Division – R. Crane, M. Foley
- Advanced Composite Office, Hill AFB and Air Force Research Lab
  - Larry Coulter, Ken Patterson, Lt. Dane Morgan, Frank
- Resin Suppliers: Applied Poleramics, Inc., Ashland, Hexion, Corezyn
- ESTCP WP-0617, SERDP PP-1271, EQBRD, SPOTA for funding

Low VOC Resin Technology

Low Cost and High-Impact Environmental Solutions for Composite Structures

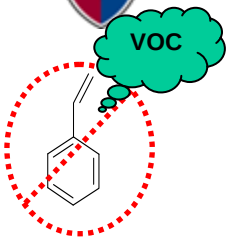
Need for Low VOC Resins

Liquid resins used in molding large-scale composites are a significant source of Volatile Organic Compound (VOC) emissions. In fact, the composites industry only consumes 9% of the styrene, but produces 79% of the emissions. For this reason, the EPA has enacted the Reinforced Plastic Composites NESHAP, which mandates the maximum HAP content in liquid molding resins.

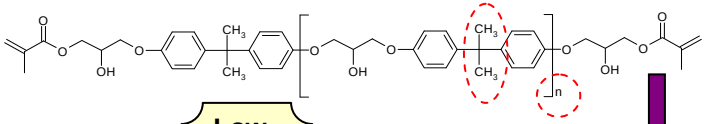


Solutions

- **Fatty acid monomers as styrene replacements**
- **Tailor molecular structure of vinyl ester monomers**



Soybeans



Low VOC Resin

Resin Processing

- Low viscosity
- VARTM, SCRIMP, SMC capabilities

Composite hood

Polymer Properties

- High T_g, strength, toughness
- Comparable to commercial resins

Applications

Applicable to all uses of unsaturated polyesters and vinyl esters, including all methods of manufacture.

- **Military vehicles and structure**
- **Automobile parts**
- **Boats**
- **Gel coats**

Facilities

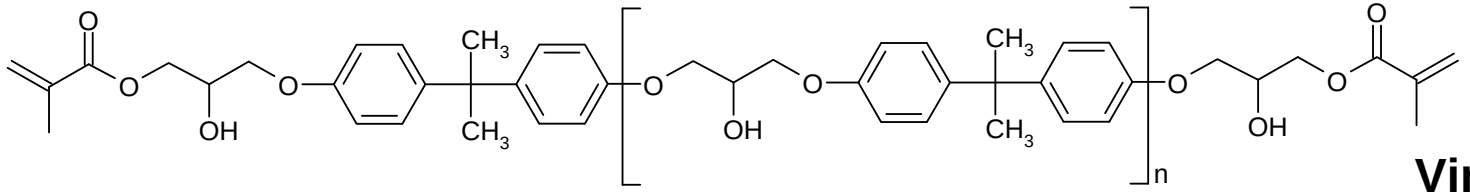
Army Research Laboratory
Rodman Materials Building
APG, MD

Drexel University
Philadelphia, PA

TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

To discuss licensing this technology, contact: Professor Giuseppe R. Palmese, Drexel University, Department of Chemical Engineering, Philadelphia, PA 19104, 215-895-5814, palmese@cbis.ece.drexel.edu

Low HAP Fatty Acid Vinyl Ester Resins (FAVE)

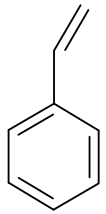


Vinyl Ester

Commercial Resins

Low VOC ~ 33 wt% Sty

Standard ~ 40-50 wt% Sty



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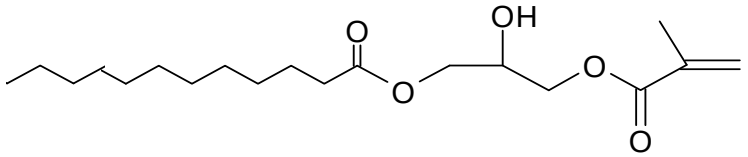


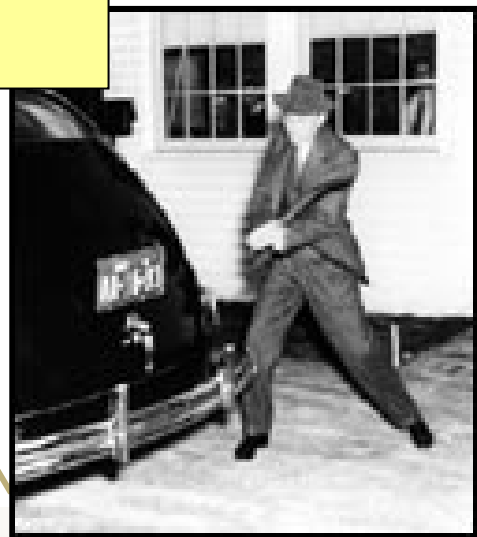
Styrene

10-25 wt%

MFA – methacrylated fatty acid

FAVE: Fatty Acid-Based Vinyl Ester Resin

- **Use fatty acid monomers to reduce styrene content**
  - **Non-volatile and inexpensive**
  - **Copolymerizes with styrene and vinyl ester**
  - **Soluble in VE and UPE**
  - **Increases renewable content in polymers**
  - **Reduces VOC/HAP emissions by 55-78%**

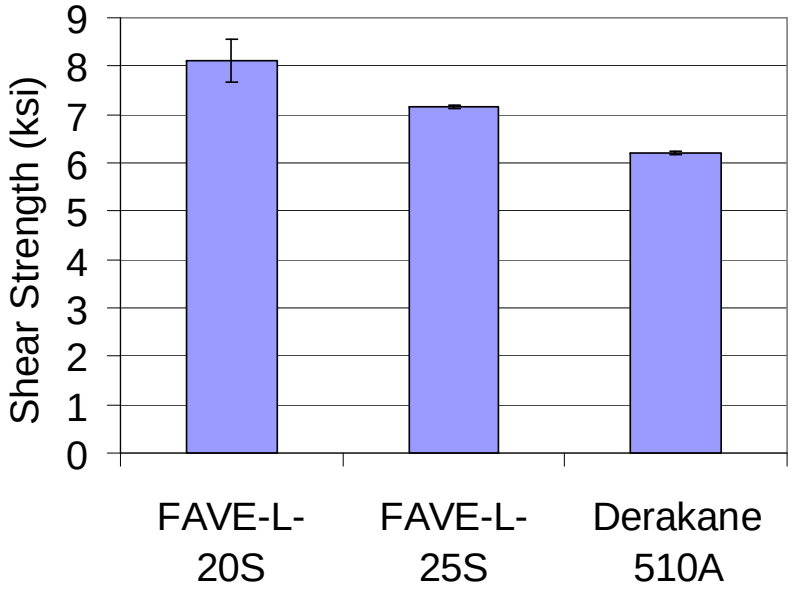


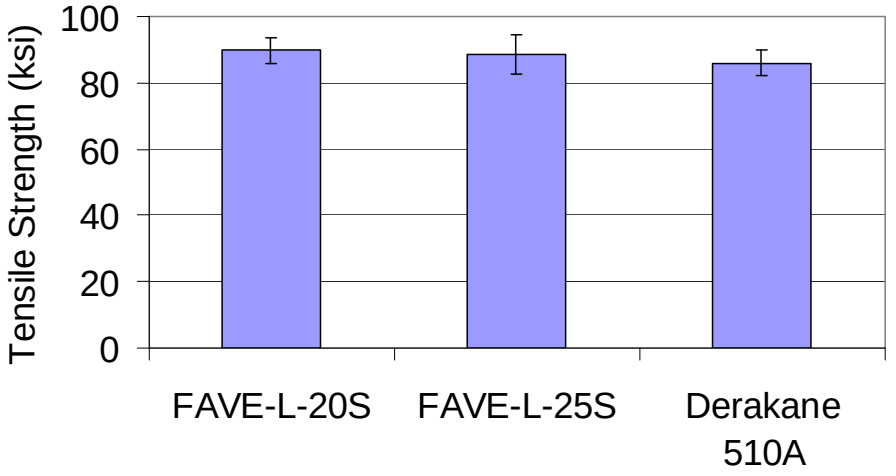
Resin and Fabric Reinforcement

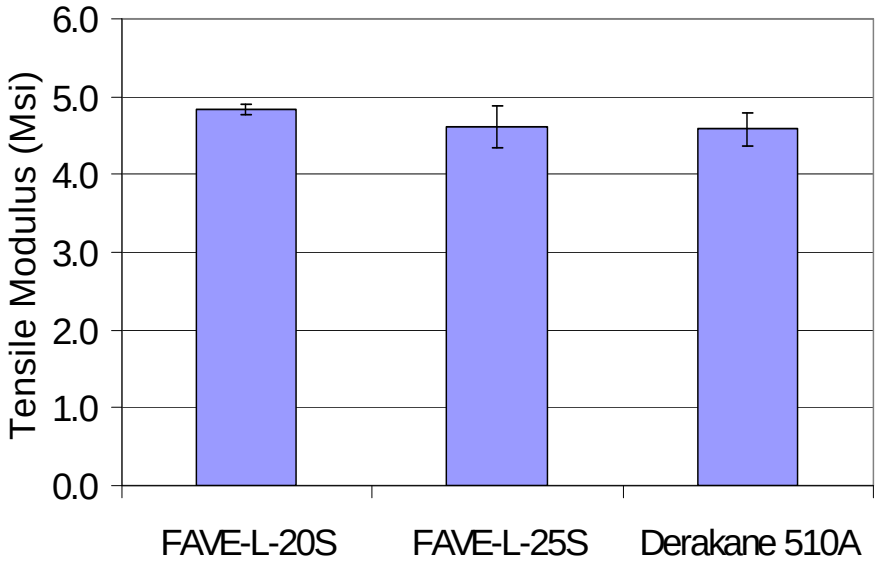
Application	Fabric	Resin	Resin Replacement
Amtech Helmet Hardtop	3-Tex 100 oz S2-glass and 24 oz S2-glass	Derakane 8084	FAVE-O-25S
HMMWV Hood	3D E-glass	Hetron 980-35	FAVE-L-HT/O-HT
M35A3 and M939 Hood	3-Tex 96 oz E-glass	Hetron 980-35 (VE) or Huntsman 8605 (Epoxy)	FAVE-L-HT/O-HT
Transmission Container	3-Tex 54 oz E-glass	Derakane 8084	FAVE-L-25S/O-25S
T-38 Dorsal Cover and F22 Canopy Cover	Fibre Glast Developments Corp. 120 3 oz E-glass and Style 7781 E-glass 9 oz	Hexion 781-2140	FAVE-L-25S/O-25S
Rudders	Fiber Glass Ind. 18 oz E-glass	Corezyn Corve 8100 and Derakane 510A-40	FAVE-L-25S

- **Derakane 8084:** **~40 wt% styrene**
- **Hexion 781-2140:** **47 wt% styrene**
- **Corve 8100:** **50 wt% styrene**
- **Hetron 980/35** **<35% styrene**
- **Derakane 441-400:** **33 wt% styrene (low HAP resin)**
- **FAVE-L/FAVE-O-25S:** **25 wt% styrene, L – methacrylated Lauric acid**
  O – methacrylated Octanoic acid
- **FAVE-O-HT:** **25 wt% styrene, Novolac VE**

FAVE Meets Navy Composite Panel Validation







- **Both FAVE-L and FAVE-L-25S are similar or exceed performance of commercial resins**
- **Toughness alone decreased, but this was likely due to incomplete cure**

FAVE-O-25S and FAVE-L-25S Performance

Property	Strength (ksi)	Requirement (ksi)	Modulus (msi)	Requirement (msi)
FAVE-O-25S 4 pt bend Room Temp	**62.0**	**55.0**	**3.70**	**3.70**
FAVE-O-25S Short beam shear Room Temp	**4.80**	**4.50**	**-**	**-**
FAVE-L-25S 4 pt bend Room Temp	**70.0**	**55.0**	**3.85**	**3.70**
FAVE-L-25S Short beam shear Room Temp	**5.10**	**4.50**	**-**	**-**

- **FAVE-O-25S and FAVE-L-25S meet specs for Army transmission containers and HMMWV hardtop**

FAVE-O-HT Performance

	Batch 2 Strength (ksi)	Batch 1 Strength (ksi)	Require-ment (ksi)	Batch 2 Modulus (msi)	Batch 1 Modulus (msi)	Require-ment (msi)
4 pt bend Room Temp	**62.0**	**56.6**	**55.0**	**3.76**	**3.67**	**3.70**
4 pt bend 250 F	**36.2**	**29.3**	**30**	**2.9**	**2.69**	**3.0**
Short beam shear Room Temp	**4.08**	**3.70**	**4.50**	-	-	-
Short beam shear 250 F	**3.20**	**2.90**	**3.0**	-	-	-

- **Reformulated (Batch 2) FAVE-O-HT meets specs for Army hoods.**

M35A3 Hood Validation

Impact 4 – large radius corner

- No permanent deformation.
- No separation of reinforcements from the hood.
- No cracks.
- Test passed.

Impact 5, 6 – Small radius corner

MCM Rudder Fabrication

Installation of Vertical Shear Ties

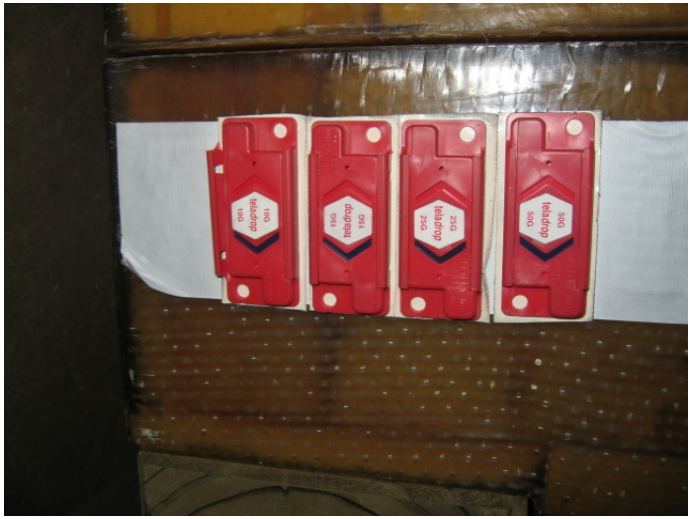
After Infusion of
Vertical Shear Ties

MCM Rudder Fabrication

During infusion of first packet (5 layers)

After infusion of first packet

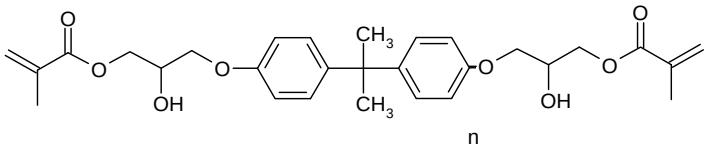
Container Testing



M35A3 Hood

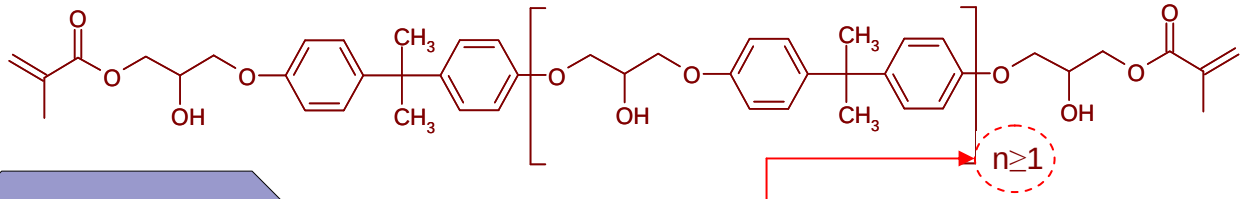
- **The major steps in hood production are:**
  - **cut 3Tex 96 oz main ply**
  - **stiffeners consisting of a foam core and wrappping ply are purchased pre-cut**
  - **lay-up plies and stiffeners. Place additional reinforcement plies over the stiffeners and along the perimeter of the hood**
  - **bag part**
  - **mix resin, CoNap, and MEKP and infuse with FAVE-L vinyl ester resin or vantico 8605 epoxy resin**
  - **post-cure part**
  - **trim hood in router**
  - **drill holes for hardware**
  - **bond safety latch and handles**

Bimodal Vinyl Ester Resins (BM-VE)



Low Molecular Weight VE

High Molecular Weight VE



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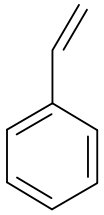


Styrene

Reduces Styrene content to 28-38 wt.%

VE molecular weight affects resin and polymer properties

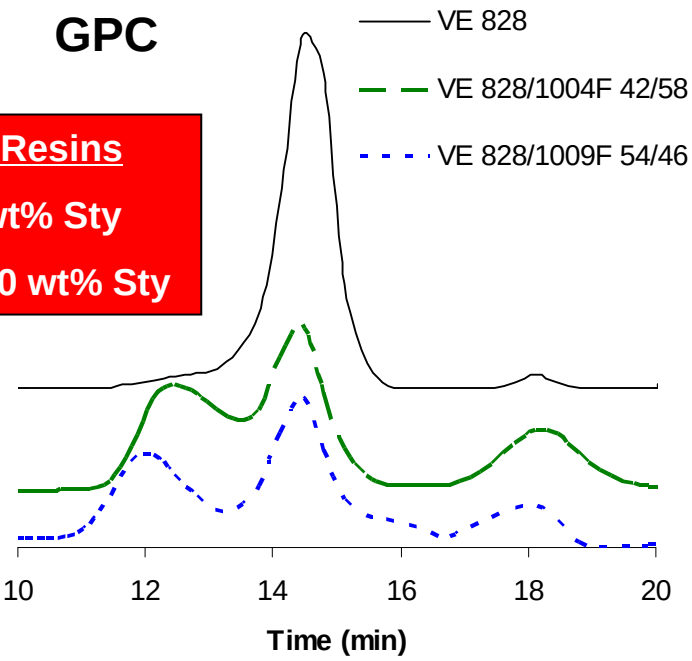
- **Low VE molecular weight**
  - **Low viscosity**
  - **Low fracture properties**
- **High VE molecular weight**
  - **High viscosity**
  - **High fracture properties**

Commercial Resins

Low VOC ~ 33 wt% Sty

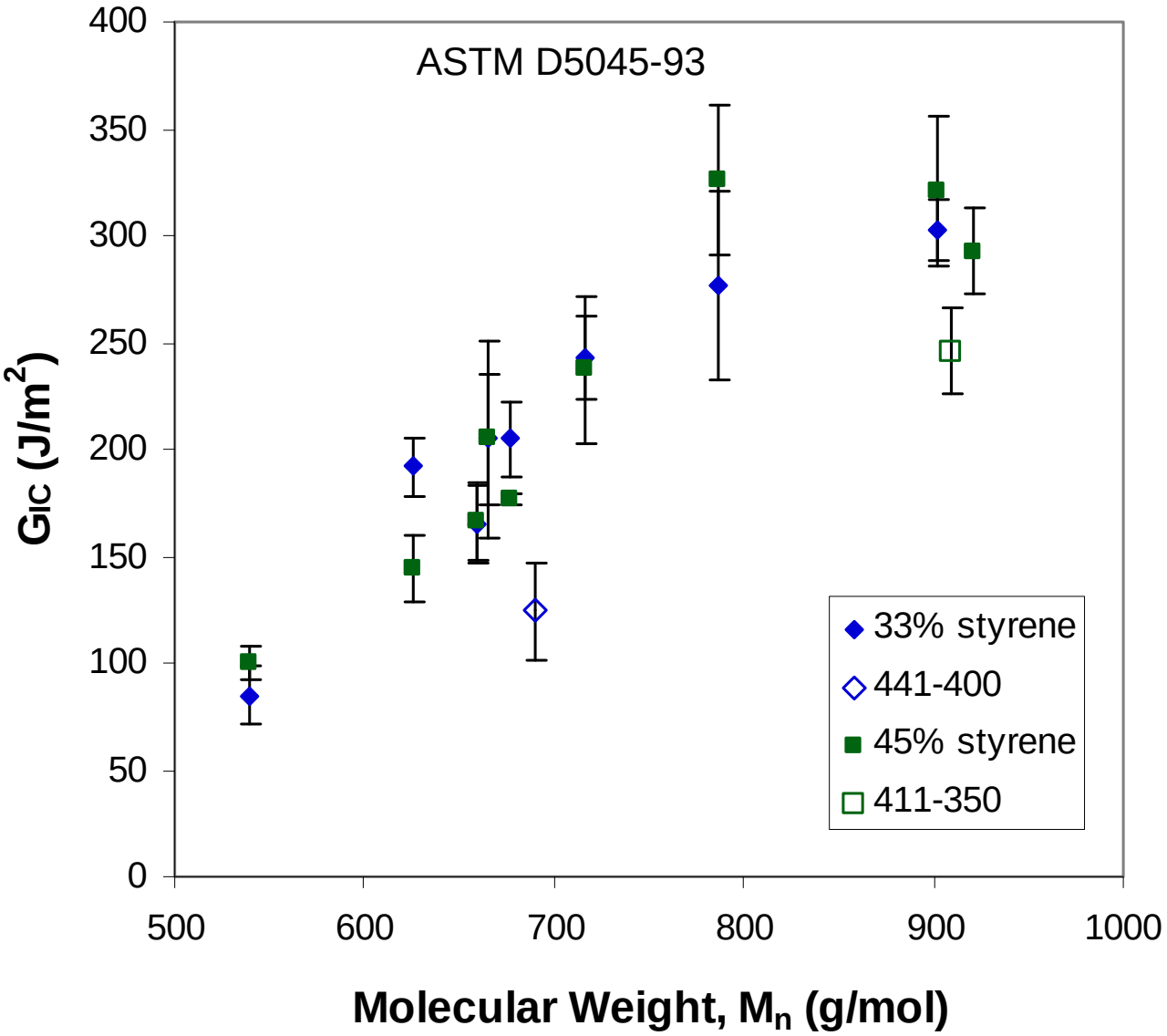
Standard ~ 40-50 wt% Sty

GPC



*** Source: ARL/Drexel patent application, April 2005.**

Improved Fracture Properties of Bimodal Resins



- **Bimodal resins have superior fracture properties**

Bio-based Rubber (BR) Toughening Agents

- **Designed plant oil-based toughening agents**
- **Uses phase separation to capture MFA reactive diluent**
- **Increases toughness while decreasing styrene content and maintaining viscosity**